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POLARIZED INFRARED SPECTRAL STUDIES OF CRYSTALLINE, HYDROGEN-BOND--ETC(U)

MAY 77 J E KATON, P F KRAUSE, K K SMITH

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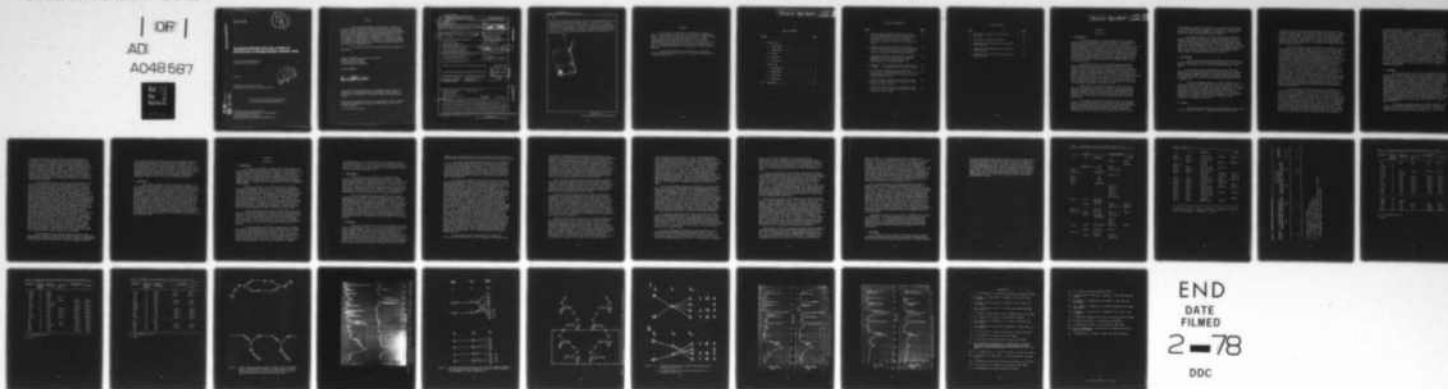
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# **POLARIZED INFRARED SPECTRAL STUDIES OF CRYSTALLINE, HYDROGEN-BONDED ORGANIC ACIDS**

*ANALYTICAL SERVICES BRANCH  
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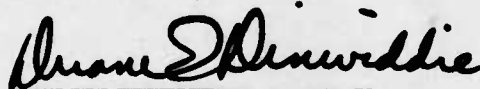
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DUANE E. DINWIDDIE, Capt, USAF, Acting Chief  
Analytical Services Branch  
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Air Force Materials Laboratory

FOR THE COMMANDER

A handwritten signature in dark ink, reading "Duane E. Dinwiddie", is written over a horizontal line.

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## FOREWORD

This report was prepared by the Department of Chemistry, Miami University, Oxford, Ohio under Air Force contract #F33615- 73-C-5013. This contract was initiated under Project No. 7360, "Chemical, Thermal and Dynamic Properties of Materials", Task No. 736005, "Compositional, Atomic and Molecular Analysis". The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Major J. H. Hauschild and Major K. E. Siegenthaler served as Project Engineers.

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## SECTION I

### ACRYLIC ACID

#### 1. Introduction

The striking effects on vibrational spectra due to hydrogen bonding have been the subject of many investigations. The general spectral features associated with such spectra are well documented, but neither detailed spectral interpretations nor truly satisfactory theoretical interpretations are as yet available. Polarized infrared spectroscopy has been used only to a moderate extent in vibrational analyses and solid state structural studies. The advantages of this technique, along with the observation that many compounds form highly-oriented polycrystalline films when grown between alkali halide plates, indicates that utilizing the polarized infrared technique with compounds known to hydrogen bond in the solid may lead to further progress in the understanding of their vibrational spectra.

In accord with this, we have been investigating the solid phase infrared spectra of a number of carboxylic acids because of an interest in their structures in condensed states and in the interpretation of their vibrational spectra. Organic acids hydrogen bond rather strongly and may form either hydrogen-bonded dimers or hydrogen-bonded polymers in their condensed states [1-3]. Both of these structures are shown for reference in Fig. 1. It should be noted that the polymer structure shown is given only for comparison purposes, since acrylic acid is not known to form this structure. Both of these basic structures have two or more substructures which are possible, each differing from the others by the detailed conformation of the monomer units.

Structurally, the vibrational spectra of most liquid acids can be best interpreted on the basis of dimeric ( $C_1$  or  $C_{2h}$ ) molecular symmetry. Although this interpretation offers reasonable consistency with the chemistry of such systems and with the group theoretical predictions, the selection rules have been empirically shown not to be rigorous [4]. In this paper we report the infrared spectra of solid acrylic acid.

In attempting to further understand the effects of hydrogen bonding on the vibrational spectra of carboxylic acids, acrylic acid seems a particularly wise choice since (a) its liquid phase vibrational spectra have been reported and interpreted in terms of  $C_{2h}$  dimeric symmetry [4]; (b) the crystal structure of acrylic acid has been determined from x-ray diffraction studies [5,6]; and (c) it is one of

the simplest acids known to be dimeric in the solid, which is presumed to be the most common type structure for these acids. Since the x-ray results are known, we have examined the consistency of solid state structural results using polarized infrared spectra.

The crystal structure of acrylic acid has been reported by two different groups of workers [5,6]. Both determinations, one performed at 203°K and one performed at 138°K, show the acid crystallizes in the orthorhombic system, space group  $D_{2h}^{26}$  (Ibam), with eight monomer units in the crystallographic unit cell. The crystallographic  $c$  axis is parallel to the  $z$  molecular axis with a center of symmetry between monomer units. The structure, therefore, consists of planar hydrogen-bonded dimers lying on  $C_{2h}$  sites with two such units in the Bravais cell, or alternatively, four monomer units located on  $C_s$  sites.

## 2. Experimental

Acrylic acid was purchased from Matheson, Coleman and Bell and was distilled in vacuo prior to every sample preparation. The fraction boiling at 27°C under a 4 torr vacuum was collected and used in this work.

Our approach to this investigation has been eased by the development of techniques whereby one may grow oriented polycrystalline films of organic compounds suitable for infrared polarization studies. The methods and sample cell employed for growing oriented polycrystals of compounds that are liquids at room temperature have been described previously [7].

Acrylic acid rapidly polymerizes at room temperature once the inhibitor is removed by distillation, and therefore, oriented polycrystalline films were grown immediately after distillation of the liquid. The sample was placed in a closed cycle Cryogenic Technology Inc. Model 20 Cryostat and cooled to a nominal temperature of 20°K, at which temperature the mid-infrared spectra were recorded. The spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer. The reported frequencies are thought to be accurate to  $\pm 1 \text{ cm}^{-1}$  with reproducibilities of better than  $\pm 0.5 \text{ cm}^{-1}$ .

## 3. Results

Typical polarized infrared spectra of crystalline acrylic acid at 20°K are shown in Figure 2. Temperature dependent spectra were

recorded from near the melting point (284°K) to 20°K. The spectra were essentially identical with those shown in Figure 2 indicating no apparent solid-solid phase change. The difference between the two spectra shown is due to a 90° rotation of the polarizer. Each band gave maximum and minimum intensities at these polarizer settings. The spectra indicate a high degree of sample orientation. The frequencies corresponding to the observed bands along with the liquid phase infrared and Raman frequencies [4] are given in Table 1.

The spectra shown in Figure 2 exhibit only two types of polarization which, for a general sample orientation, are inconsistent with an orthorhombic crystal system. A general orientation of an orthorhombic crystal predicts three types of polarization behavior [8]. The in-plane A' modes ( $C_s$  molecular symmetry) are assigned to the upper trace while in the lower trace these modes are nearly extinguished and the A'' modes are maximized. The single solid state component observed for the A' modes is in disagreement with the factor group analysis prediction of two (see below). If we assume the oriented polycrystalline film has the same structure as that determined by the x-ray diffraction, and there is no reason to believe it is not, these results are indicative of the orientation of the crystal with respect to the substrate. In order not to observe one of the unit cell modes of an orthorhombic crystal, it is necessary that the infrared radiation be normal to a crystal face which can be described by a set of Miller indices where two of the three indices are zero. Since the  $z$  molecular axis ( $B_{1u}$  representation of the  $D_{2h}$  factor group) is parallel to the  $c$  crystal axis, the crystallographic face perpendicular to the beam is either the (010) or (100) plane. This requires that either the  $B_{2u}$  or the  $B_{3u}$  symmetry species of the  $D_{2h}$  factor group be not observed since the dipole moment change for one of them must necessarily be oriented along the direction of propagation of the infrared radiation.

Since the polarized spectra shown in Figure 2 separate the in-plane A' and out-of-plane A'' vibrational modes, partial confirmation of the vibrational assignments made on the basis of the liquid phase infrared and Raman spectra [4] is obtainable. In particular, the rather tentative assignments of the out-of-plane modes of acrylic acid (with the exception of the -OH out-of-plane mode at 925  $\text{cm}^{-1}$ , which is obvious from the liquid spectrum) may now be confirmed. First of all, the assignments of the three out-of-plane CH modes of the vinyl group may be considered. A strong band in the liquid infrared spectrum at 984  $\text{cm}^{-1}$  was assigned to both the  $\text{CH}_2$  twist and wag, these being accidentally degenerate. The degeneracy is removed in the polycrystalline spectrum and the two bands, one at 991  $\text{cm}^{-1}$  ( $\text{CH}_2$  twist) and one at 975  $\text{cm}^{-1}$  ( $\text{CH}_2$  wag), are both maximized in the lower trace of Figure 2 indicating that both modes have

out-of-plane character. The third CH out-of-plane bend of the vinyl group had been assigned to a band at  $819\text{ cm}^{-1}$  in the liquid. Potts and Nyquist [9] state that although it is not a good group frequency, the mode is likely to be around  $580\text{ cm}^{-1}$ . The assignment of the  $819\text{ cm}^{-1}$  band was thought, therefore, to be questionable. The band at  $819\text{ cm}^{-1}$  in the lower trace of Figure 2 clearly identifies it as the correct choice. The data also confirm the assignments of the  $\text{CO}_2$  deformations at  $535$  and  $505\text{ cm}^{-1}$  in the solid ( $525$  and  $512\text{ cm}^{-1}$  in the liquid phase). The higher frequency band is readily assigned as the in-plane deformation ( $\text{CO}_2$  rock) and the lower frequency component as the out-of-plane bend ( $\text{CO}_2$  wag). This order of the rock being higher in frequency than the wag is the reverse of that found in acetic acid [10,11]. A band at  $336\text{ cm}^{-1}$  in the liquid spectrum was assigned as a skeletal deformation. Since it is maximized in the upper trace of Figure 2 and totally absent in the lower spectrum, it must be assigned to an in-plane mode. Finally, in the liquid, the infrared active OH bend was assigned to a strong band at  $1297\text{ cm}^{-1}$  while the C-C stretch was assigned to a band at  $1240\text{ cm}^{-1}$ . From the observed intensities in the solid (the  $1258\text{ cm}^{-1}$  band is much stronger than the  $1302\text{ cm}^{-1}$  band), it appears that these assignments should be interchanged.

#### 4. Discussion

The approach we have used for the interpretation of the solid state polarized infrared spectra is basically the correlation method of Fateley, et al. [12]. The Bravais unit cell is composed of four monomer units located at sites of  $C_s$  symmetry, or alternatively, two hydrogen-bonded dimer units located at  $C_{2h}$  sites. Because of the nature of this system one may envision two possible approaches to the interpretation of the vibrational spectra: (1) an interpretation based on a primitive cell composed of two weakly interacting dimer molecules, or (2) an interpretation based on four monomer molecules, some of whose modes are highly perturbed by hydrogen-bonding to a nearest neighbor molecule. In the second case, other intermolecular interactions are assumed to be much smaller. This approach is similar to that employed by Millikan and Pitzer [13] in discussing the crystal spectrum of formic acid which exists as a hydrogen-bonded polymer in its most stable polymorphic form. The correlation diagrams for the factor group analysis for both cases are shown in Figure 3.

As the dimeric structure possesses a center of symmetry, its vibrational spectrum is somewhat easier to interpret. However, the details of the spectra still present a problem. This is particularly apparent when one considers the liquid phase spectra. They appear to

be most consistent with a dimer structure, but possibly because of asymmetry of the potential field which the molecule experiences in the liquid state, the selection rules do not hold rigorously. One formally expects no coincidence between Raman and infrared bands when a molecule possesses a center of symmetry. Indeed there does exist non-coincidences in the liquid spectra. A strong infrared band at  $1705\text{ cm}^{-1}$  has no Raman counterpart. Strong Raman bands are observed at  $1660\text{ cm}^{-1}$  and  $1395\text{ cm}^{-1}$  with no counterparts in the infrared. Other examples may be derived from Table 1. On the other hand, a number of bands are observed in both the infrared and Raman spectra, but with a large intensity reversal. This breakdown in selection rules makes the assignment more difficult.

The correlation diagrams shown in Figure 3 both predict that the in-plane modes ( $A'$  of  $C_s$  and  $B_u$  of  $C_{2h}$ ) should give rise to two infrared active crystal bands. The out-of-plane modes ( $A''$  of  $C_s$  and  $A_u$  of  $C_{2h}$ ), on the other hand, should give rise to only one infrared active crystal band. The observation of only one component for each species has been discussed earlier. One may argue that the bands which appear in the crystal spectrum which are not readily apparent in the liquid spectrum, e.g., bands at  $1680$ ,  $1520$ ,  $1505$ ,  $1380$  and  $1320\text{ cm}^{-1}$ , are actually the missing factor group components. However, the polarization behavior of these bands is identical to that of the nearby fundamentals. Such results are consistent with the known crystal structure if an  $(hk0)$  face is perpendicular to the infrared beam, however, the frequencies of these bands are so different from the nearest fundamentals that their explanation as factor group components is unreasonable. The first three bands would require factor group splittings of  $40$ ,  $94$  and  $63\text{ cm}^{-1}$ , respectively. The fourth would require that two fundamentals were accidentally degenerate plus a factor group splitting of  $14\text{ cm}^{-1}$  and the fifth would require a factor group splitting of  $21\text{ cm}^{-1}$ . Such large splittings would require extremely large intermolecular interactions and do not seem reasonable for a dimer molecule with zero dipole moment. These new bands must, therefore, be due to combination modes. It is important to note that although some new bands appear in the solid spectrum because of the better resolution afforded by the low temperature and the polarizer, a few bands that were weak in the infrared spectrum of the liquid with strong Raman counterparts disappear in the solid infrared spectrum. This indicates that the selection rules hold more rigorously in the crystal, at least for these modes.

The broad band at about  $3200\text{ cm}^{-1}$  which is present in both spectra shown in Figure 2 is the only band present which is not essentially extinguished at one polarizer setting or another. A number of explanations can be proposed for this observation. The most satisfying accounts for

it as arising from water present in the acrylic acid sample, which was not removed by purification. The removal of small amounts of water which are present in many low molecular weight carboxylic acids, is extremely difficult. This is particularly true of acrylic acid since it is so prone to polymerize. Blank experiments were carried out to make certain that the band was not due to a leak in the vacuum system. Other explanations involve ascribing non-linearity to the hydrogen bond or combination bands with the -OH stretching fundamental that have the appropriate symmetry. These are at best, speculative arguments.

## 5. Conclusion

The following conclusions may be drawn from this study: (1) the polarized infrared spectra of acrylic acid films are consistent with the reported crystal structure. This result helps point out the usefulness of using the polarized infrared technique for solid state structural investigations, particularly of compounds that are liquids at room temperature. (2) It makes no real difference in this case whether the spectra are interpreted in terms of monomer units on  $C_s$  sites or dimer units on  $C_{2h}$  sites. It may be that this arises from the fact that both the dimeric molecular symmetry and its site symmetry are the same ( $C_{2h}$ ), and the monomeric molecular symmetry and its site are identical ( $C_s$ ). The case where this is not true is presently under consideration. (3) The segregation of the in-plane and out-of-plane vibrational modes of acrylic acid through the polarized infrared spectra has led to a rapid confirmation for most of the assignments proposed for the liquid spectrum. In addition, in cases where clarification of assignments were needed or where additional bands were observed, this technique allows classification to be made with ease.



## SECTION II

### ACETIC ACID

#### 1. Introduction

It is well established that organic acids of fairly high molecular weight crystallize as hydrogen bonded dimers. We have investigated the polarized infrared spectrum of a number of these acids [2,3,14] and have found the increased resolution afforded by this technique extremely useful in making vibrational assignments as well as in making arguments concerning structural details. An alternative structure of organic acids in the solid state is a long polymeric chain of hydrogen-bonded monomers. Formic acid [15] and acetic acid [16,17,18] crystallize in this manner.

Millikan and Pitzer [13] have concluded from the infrared spectrum of crystalline formic acid that it can best be interpreted on the basis of a molecular chain unit cell. Their description assumes a one dimensional lattice for formic acid from which a two molecule Bravais cell [19] can be determined. The implications of this interpretation are that the "weak" Van der Waal's interactions between the two chains in the crystallographic unit cell are neglected. The Millikan and Pitzer [13] detailed analysis of the crystalline spectrum of formic acid has been shown [20] to be incorrect because of polymorphism in crystalline formic acid [21]. The underlying assumption of a two molecule Bravais cell in which the interchain interaction is neglected has been used in a normal coordinate treatment of formic acid, [22] however.

In analyzing the polarized infrared crystal spectra of acrylic acid, [14] which crystallizes with a dimeric structure, we attempted to interpret the results considering the structure as two interacting dimer units or as four monomer units whose interactions significantly perturbed the crystal spectrum particularly in the case of the hydrogen bond interaction. In the case of acrylic acid, although the results may have been fortuitous, the alternative approaches give identical predictions.

It therefore seemed worthwhile to investigate the situation with an acid that crystallized as a hydrogen bonded polymer. We therefore present the polarized infrared spectra for acetic acid and two of its deuterated derivatives  $\text{CD}_3\text{COOD}$  and  $\text{CH}_3\text{COOD}$ . Acetic acid is isomorphic with formic acid [15-18] and we feel that many of the arguments that are valid for crystalline formic acid should also hold for crystalline acetic acid. The method we have employed to distinguish spectroscopically between the chain Bravais model and the normal



crystallographic unit cell interactions is the correlation method described by Fateley, et al. [12] The acetic acid system seems particularly suitable for such a study because of the experimental infrared [23,11,24] and Raman data [25] available as well as theoretical calculations concerning the structure. [21]

## 2. Experimental

Water existing as an impurity in low molecular weight carboxylic acids is very common and extremely difficult to remove. Before sample preparation, attempts were made to purify the acetic acid (99.8% assayed purity) by drying over  $\text{CaSO}_4$  for two periods of forty-eight hours each, and then distilling from  $\text{CaSO}_4$ . As a check on the purity of the sample, a mid-infrared survey scan was run on the liquid and showed no bands other than those reported for liquid  $\text{CH}_3\text{COOH}$ . [23] In addition, purifications were also carried out on the  $\text{CH}_3\text{COOD}$  (99%, Wilmad Glass Co., Inc.) and  $\text{CD}_3\text{COOD}$  (99.5%, Bio-Rad Laboratories).

The liquid samples were then transferred to the sampling compartment of a CTi Model 20 Cryostat as capillary films and oriented polycrystals were grown by the method described previously. [7] The mid-infrared spectra were recorded at low temperatures with a Perkin-Elmer Model 180 ratio recording spectrophotometer. The reported frequencies are thought to be accurate to within  $\pm 1 \text{ cm}^{-1}$  with a precision of  $\pm 0.1 \text{ cm}^{-1}$ . The interpretative ambiguities that arose because of polymorphism in formic acid [20,21] were of concern to us because of the similarities between the reported crystal structures of formic and acetic acids. It was important that the oriented polycrystals which were grown were of the same structure as that determined by the x-ray diffraction experiment. Polymorphism in acetic acid has been indicated. [21,26]

## 3. Discussion

The crystal structure of acetic acid is essentially the same as that of formic acid, [15,18], i.e., the structure exists as chains of hydrogen bonded monomers. The structures are both orthorhombic with  $\text{Pna}2_1 - \text{C}_{2v}^9$  space group symmetry, each with four molecules in the crystallographic unit cell. Figure 4 schematically represents the polymer structure of solid acetic acid. A test of our method of growing crystals between alkali halide windows was performed by studying the carbonyl stretching region and the C-O stretching region of crystalline formic acid. At least ten different films of formic acid were prepared and in each case only one strong band was observed in each of the two

regions. This is indicative of the  $\beta$  form of formic acid (the crystallographically determined structure) grown previously between CsI plates. [20]

The  $\alpha$  form, which Millikan and Pitzer grew by vapor deposition, [13] gives two strong bands in both the  $\nu\text{C=O}$  region and the  $\nu\text{C-O}$  region. We feel that the above results indicate that our method of growing crystals yields the polymorph of interest to us. By growing the acetic acid films in the same manner and observing again only one strong band in the carbonyl stretching region as well as only one band in the single bond carbon oxygen stretching region, the conclusion was made that the polymorph of acetic acid grown was the one whose crystal structure has been reported. [16,18]

The acetic acid molecules crystallize on sites of  $C_1$  symmetry and, hence, all molecular vibrations are infrared active under the site symmetry approximation. Under the assumption of  $C_s$  symmetry for an isolated acetic acid monomer, the "normal" correlation diagram for the four molecule Bravais cell is shown in the top half of Figure 5. The correlation predicts, for a general sample orientation, three infrared active factor group components for each molecular vibrational mode, each having different polarization properties. The correlation diagram for an alternative interpretation which employs the two-molecule chain unit cell of Millikan and Pitzer is shown in the bottom half of Figure 5. The predictions from this diagram are quite different from those of the "normal" correlation. In this case each molecular mode should give rise to two factor group components, with both the  $A'$  modes infrared active while only one of the  $A''$  modes will be observable in the infrared. Three distinct band polarizations should be observed for a general sample orientation. It is extremely important to note from these correlations that "normal" crystallographic unit cell interactions in the solid will split both the in-plane  $A'$  and out-of-plane  $A''$  molecular modes into observable infrared factor group components while the chain unit cell will split the  $A'$  modes into two observable infrared components while the  $A''$  modes will give rise to only one observable infrared factor group species. The observation of no infrared factor group splitting for the out-of-plane vibrational modes in the spectrum of solid formic acid has led Miyazawa and Pitzer [27] to conclude that the neglect of interchain interactions is appropriate for their treatment of the solid infrared spectra. (The identical correlation diagrams shown in Figure 5 may be formulated for formic acid). Mikawa, Brasch and Jakobsen [22] have employed the same assumption for the normal coordinate calculation in solid formic acid.

As in acrylic acid, if the molecules orient themselves between the alkali halide plates in such a manner as to have one of the

orthorhombic crystallographic axes parallel to the direction of propagation of the infrared radiation, the number of factor group components observable in the infrared is altered significantly. The predicted number of infrared factor group components for a general sample orientation just mentioned for both the "normal" four molecule Bravais cell and for the two-molecule chain unit cell are summarized in Table 2. It is important to note that since we are assuming that the acetic acid molecules crystallize in the  $C_{2v}^9$  space group symmetry between the alkali halide plates, the number of factor group components shown in Table 2 also represents the predicted unique band polarizations for each case. Included in the table for comparison are the experimentally observed number of factor group components and band polarizations.

Table 2 shows the prediction that three factor group components should be observed for both the in-plane and out-of-plane molecular species for a general sample orientation in the "normal" unit cell case whereas two unit cell components should be observed for the A' modes in the chain unit cell model and one for the A'' modes. Comparing these predictions with the number of experimentally observed components in column 6 leads to discrepancies with both models.

The fourth and fifth columns give the predictions for specific orientations of acetic acid molecules with respect to the incident radiation. The orientations indicated are those in which one of the orthorhombic crystal axes is parallel to the infrared beam. For these cases, two factor group components for both the in-plane and out-of-plane modes should be observed in the infrared for the "normal" unit cell, whereas one or two components, depending on the specific orientation, should be observed for the in-plane A' modes in the chain unit cell and zero or one infrared observable components for the A'' species in the chain unit cell. Comparing the experimental results in columns six and seven with these predictions yields a match with the normal unit cell and a specific orientation.

Figure 6 and Table 3 give the results for the polarized spectrum of crystalline acetic acid-d<sub>0</sub> at 190°K. The two traces in Figure 6 differ by a 90° rotation of the grid polarizer. The top trace is arbitrarily assigned a relative polarizer angle of  $\alpha$  while the lower trace is  $\alpha + 90^\circ$ . These orientations are those at which bands showed a maximum or minimum intensity. The frequencies corresponding to these spectra are given in Table 3. In all but three cases, the OH stretching mode, the carbonyl stretching mode at  $1653\text{ cm}^{-1}$  and a methyl rocking mode at  $1044\text{ cm}^{-1}$ , bands present in the  $\alpha$  spectrum extinguished completely in the  $\alpha + 90^\circ$  spectrum and, conversely, bands present in the  $\alpha + 90^\circ$  spectrum disappear as the polarizer is rotated by 90°. As

bands disappear in one spectrum or the other, the new bands appear close in frequency (typically  $5\text{ cm}^{-1}$  or less). This magnitude coupled with the new band polarization which follows from the correlation method, indicates that we are observing pairs of factor group components whose origin is the same molecular species. Since our experimental frequencies should be precise to  $\pm 0.1\text{ cm}^{-1}$ , the bands at  $1043.3\text{ cm}^{-1}$  ( $\alpha$  spectrum) and  $1044.0\text{ cm}^{-1}$  ( $\alpha + 90^\circ$  spectrum) could be assigned, on the basis of the  $0.7\text{ cm}^{-1}$  splitting, to different components of the  $1044.0\text{ cm}^{-1}$  methyl rock. However, we are somewhat cautious about assigning bands that differ by less than  $1\text{ cm}^{-1}$  to different bands, and prefer the evidence given below for the solid  $\text{CH}_3\text{COOD}$  spectra factor group splitting for this mode. This is of added significance, it seems, when the vibrational species in question is an out-of-plane mode because of the consequences in assigning observable splittings to such modes.

It is not particularly surprising that neither the  $-\text{OH}$  stretching mode nor the carbonyl stretching mode yield distinguishable infrared factor group components. In  $\text{CH}_3\text{COOH}$ , the  $-\text{OH}$  stretching mode is a broad strong band with frequencies  $2921 \pm 2\text{ cm}^{-1}$  in both the  $\alpha$  and  $\alpha + 90^\circ$  spectrum. The intensities, however, show significant alteration. We feel that if resolved the factor group pair would differ in frequency by a few wavenumbers. This is based on the analysis of the physical nature of the structure itself as well as analogy with the results of the formic acid normal coordinate analysis. [21] From the latter, [21] a crystal splitting of  $1\text{ cm}^{-1}$  for the  $-\text{OH}$  stretching mode is predicted. There exists low frequency shoulders at  $2665\text{ cm}^{-1}$ ,  $2614$  and  $2521\text{ cm}^{-1}$ . These bands are present in the liquid spectrum of acetic acid, indicating that they are most likely combinations. These are well known combinations in dimeric carboxylic acids and certainly not factor group components.

The carbonyl stretching mode is a fairly broad band with experimentally indistinguishable factor group components in the  $\alpha$  and  $\alpha + 90^\circ$  spectra. As in the case of the  $-\text{OH}$  stretching mode, the bands do show some intensity alteration possibly indicating bands of different factor group symmetry species. The normal coordinate treatment for formic acid indicates only a  $1\text{ cm}^{-1}$  factor group splitting for the carbonyl stretching mode and if this is appropriate for acetic acid, it is not surprising that we do not resolve the pair.

All other fundamental absorptions that were observed for solid  $\text{CH}_3\text{COOH}$  yielded experimentally observable pairs of factor group components. There is some ambiguity associated with the resolution of factor group splittings for the symmetric C-C stretch ( $911.4\text{ cm}^{-1}$ ) and the O-H out-of-plane deformation at  $\sim 908\text{ cm}^{-1}$ . This problem is addressed

below. Of particular significance is the out-of-plane CO deformation. In the  $\alpha$  spectrum a band was observed at  $588.6\text{ cm}^{-1}$ . Upon  $90^\circ$  rotation of the polarizer, this band extinguished completely, and a new band at  $593.6\text{ cm}^{-1}$  was observed. This splitting is clear indication of factor group splitting for an out-of-plane mode. This leads to the conclusion that significant interchain interactions do exist.

The polarized spectra of the deuterated derivatives lend additional support to the proposal that all vibrational modes of crystalline acetic acid are split by unit cell interactions. The polarized spectra of crystalline  $\text{CH}_3\text{COOD}$  and the associated frequencies are given in Figure 7 and Table 4. Of particular importance are the splittings observed for the OD stretch in  $\text{CH}_3\text{COOD}$  ( $\alpha$ ;  $2204.2\text{ cm}^{-1}$ ;  $\alpha + 90^\circ$ ;  $2200.5\text{ cm}^{-1}$ ) and the methyl rocking mode ( $\alpha$ ;  $1043.5\text{ cm}^{-1}$ ;  $\alpha + 90^\circ$ ;  $1044.8\text{ cm}^{-1}$ ). The corresponding vibrational modes yielded questionable factor group splitting in crystalline  $\text{CH}_3\text{COOH}$ . The splitting observed for the methyl deformation, an  $A''$  out-of-plane mode, gives additional indication of significant interchain interactions in solid acetic acid. The corresponding frequencies in  $\text{CD}_3\text{COOD}$  are  $\alpha$ ;  $924.4$ ;  $\alpha + 90^\circ$ ;  $926.0$ , further confirming these conclusions.

There are bands, however, in the spectrum of crystalline  $\text{CH}_3\text{COOD}$  that do not yield components split by  $1\text{ cm}^{-1}$  or more in the  $\alpha$  and  $\alpha + 90^\circ$  spectra. Three of these are  $A'$  modes: the carbonyl stretch, the symmetric methyl deformation at about  $1007.0\text{ cm}^{-1}$  and the carbon-carbon stretching mode at  $672\text{ cm}^{-1}$ . The weakness of the factor group interaction predicted for the carbonyl stretch along with the broadness of the band accounts for the lack of observable splittings in the spectra of solid  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOD}$ . This observation is consistent in that we were unable to resolve factor group components for this mode in the  $\text{CD}_3\text{COOD}$  spectra as well (see Table 5). Secondly, the symmetric  $\text{CH}_3$  deformation is split by less than  $1\text{ cm}^{-1}$  ( $\alpha$ ;  $1007.1\text{ cm}^{-1}$ ;  $\alpha + 90^\circ$ ;  $1006.3\text{ cm}^{-1}$ ). The observation of a  $1.6\text{ cm}^{-1}$  splitting for this mode in the undeuterated spectrum coupled with the intensity alteration evident in the polarized  $\alpha$  and  $\alpha + 90^\circ$  of  $\text{CH}_3\text{COOD}$  allows us to assign with confidence the  $0.8\text{ cm}^{-1}$  splitting to factor group interactions.

The C-C stretch raises an interesting question in both the  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOD}$  spectra. In the non-polarized  $d_0$  spectrum a broad band ( $\sim 908\text{ cm}^{-1}$ ) has associated with it a high frequency shoulder at  $911.4\text{ cm}^{-1}$ . Due to the broadness of this background we feel the majority of the intensity is due to the -OH out-of-plane mode. Therefore, the assignment of the  $911.4\text{ cm}^{-1}$  band is to C-C ( $A'$ ) and the  $\sim 908\text{ cm}^{-1}$

band to  $\gamma\text{OH}$  ( $A''$ ). In the polarized  $d_0$  spectra three bands are observed:  $908.9\text{ cm}^{-1}$ , ( $\alpha$  spectrum) and  $911.6\text{ cm}^{-1}$ ,  $897.1\text{ cm}^{-1}$  ( $\alpha + 90^\circ$  spectrum). We have assigned the  $897.1\text{ cm}^{-1}$  to one component of  $\gamma\text{OH}$  because of its intensity relative to the  $911.6\text{ cm}^{-1}$  band (which is assigned to  $\nu\text{C-C}$ ). The single band at  $908.9\text{ cm}^{-1}$  is assigned to accidentally degenerate components of both the  $911.6$  and  $897.1\text{ cm}^{-1}$  band. We would prefer, on the basis of intensity arguments, to assign the single band at  $908.0\text{ cm}^{-1}$  in the  $\alpha$  spectrum to be due to the other  $-\text{OH}$  out-of-plane factor group component, but would have no explanation for the missing carbon-carbon stretching mode component. The magnitude of this splitting ( $12\text{ cm}^{-1}$ ) for the observable components of the out-of-plane  $-\text{OH}$  deformation is of the same order as that observed for the splitting of the in-plane  $-\text{OH}$  deformation ( $16\text{ cm}^{-1}$ ).

We, therefore, feel that the intensity alteration observed in  $\text{CH}_3\text{COOD}$  for both the carbon-carbon stretching mode ( $854.6\text{ cm}^{-1}$ ;  $\alpha$  spectrum;  $855.1\text{ cm}^{-1}$ ;  $\alpha + 90^\circ$  spectrum) and the  $A''$  out-of-plane OD bend ( $671.8\text{ cm}^{-1}$ ;  $\alpha$  spectrum and  $672.1\text{ cm}^{-1}$ ;  $\alpha + 90^\circ$  spectrum) is indicative of the bands in the two spectra arising from different symmetry species in the factor group. We have no explanation for the decrease in the magnitude of interaction as the carboxylic hydrogen is replaced with deuterium. The other molecular mode in the crystalline  $\text{CH}_3\text{COOD}$  spectra which did not yield splittings greater than  $1\text{ cm}^{-1}$  was the out-of-plane  $\text{CO}_2$  deformation. In the  $\alpha$  spectrum a band was observed at  $581.7\text{ cm}^{-1}$  and in the  $\alpha + 90^\circ$  spectrum at  $582.4\text{ cm}^{-1}$ . The splitting of  $0.7\text{ cm}^{-1}$  along with the intensity changes observed in going from the  $\alpha$  to the  $\alpha + 90^\circ$  spectrum coupled with the fact that a  $5\text{ cm}^{-1}$  splitting was observed in the  $d_0$  spectra lends credence to the assignment of the pair as arising from unit cell interactions and, in particular, those between the chains.

The polarized spectra of the  $d_4$  derivative ( $\text{CD}_3\text{COOD}$ ) were recorded for completeness. The frequencies observed for this compound are given in Table 5. The spectra yielded no new information but did substantiate some of the arguments presented above. The number of observable factor group components remained constant and all bands yielded significant intensity changes as the polarizer was rotated through  $90^\circ$ .

#### 4. Conclusions

The increased resolution afforded by polarized infrared spectral techniques has allowed us to reach a new conclusion concerning interactions in solid state polymeric carboxylic acids. Our results indicate



that both interchain and intrachain interactions must be considered when describing the primitive cell in solid acetic acid. The results are consistent only with a four molecule Bravais cell which is identical to the crystallographic unit cell. The manner in which the acetic acid crystals orient themselves with respect to the alkali halide substrates is extremely fortunate in that one factor component for all species is not observed. This allows resolution of the other two. For a general sample orientation, the third component might complicate the spectra sufficiently so as not to allow the resolution of more than a single distinguishable species.

Table 1. Vibrational Frequencies of Acrylic Acid (in  $\text{cm}^{-1}$ )

Liquid <sup>4</sup>			Oriented Crystals	
R	IR	Assignment	$\theta$	$\theta + 90^\circ$
			3221.2 s	3221 s
				$\sim 3145$ sh
	3200-2500 s, vb	$\nu\text{OH}$	$\sim 3125$ s	
3112 m		$\nu\text{CH}_2$	30.95.0 w, sh	
3076 w, sh		combination		
			3068.8 w, sh	
3039 s, P		$\nu\text{CH}_2$		
2998 w		$\nu\text{CH}$		
2935 w		combination		
			1983.4 vw	
			1955.0 w	
			1947.8 w	
			1800.0 w	
			1745.5 m, sh	
1728 m	1725 m	$\nu\text{C}=\text{C}$ (op), overtone		
	1705 vs	$\nu\text{C}=\text{O}$ (op)	1720.2 s	$\sim 1720$ vw
			1680.1 m, sh	$\sim 1680$ vw
1660 s, P		$\nu\text{C}=\text{O}$ (ip)		
1637 vs. P	1636 s	$\nu\text{C}=\text{C}$ (ip)	1634.3 s	1635 w
	1617 s	$\nu\text{C}=\text{C}$ (op), combination	1616.3 w, sh	
			1522 w	
			1507 w	
1434 m	1432 s	$\nu\text{CH}_2$ scissors	1441 m-s	1441 w
	1413 m	$\nu\text{C}-\text{O}$ (op)	1396.5 m	
1395 s, P		$\nu\text{C}-\text{O}$ (ip)		
	1384 w	$\nu\text{CH}$ bend	1382.5 m	
			1323.5 w-m	



Table 1. (con't.)

R	IR	Assignment	0	$\theta + 90^\circ$
1295 w	1297 s	OH bend (op)	1302.3m	1302.7 vw
1280 s, P	1279 m	OH bend (ip)		
	1240 s	$\nu$ CC (op)	1258.5 s	1258.5 w
1232 m, P		$\nu$ CC (ip)		
1069 m	1068 m	CH <sub>2</sub> rock (op)	1077.8 m	
1048 m	1046 m	CH <sub>2</sub> rock (ip)		
977 m	984 s	CH <sub>2</sub> twist,	993.0 vw	993.4 vs
		CH <sub>2</sub> wag	975.5 vw	976.0 vs
928 w	925 m	OH bend (op)	~898 vw	896.8 vs
861 s, P	864 m	OH bend (ip)	876.0 w-m	
820 m	810 m	CH bend	815.7 w	815.7 s
643 m	650 m	CO <sub>2</sub> def (op)	655.6 m	655.8 w
625 m	628 w	CO <sub>2</sub> def (ip)		
548 w	552 w	CCO bend (op)	534.8 m	534.5 vw
525 m	525 w	CCO bend (ip)		
512 m	512 w	CO <sub>2</sub> wag		505 w-m
337 m	336 m	skeletal def	355.6 m	

s = strong, v = very, w = weak, m = medium, ip = in-phase, op = out-of-phase, P = polarized, sh = shoulder,  $\nu$  = stretch

Table 2. Factor Group Component Predictions

Table 2. Factor Group Component Reductions					
Vibrational Species <sup>a</sup>	General Sample Orientation		XOO, OXO, OOX Orientation <sup>b</sup>		Experimental
	Chain Unit Cell <sup>c</sup>		Chain Unit Cell <sup>d</sup>		
	Normal Unit Cell <sup>e</sup>	Chain Unit Cell <sup>d</sup>	Normal Unit Cell <sup>c</sup>	Chain Unit Cell <sup>d</sup>	
	$F_p^e$	$F_p^e$	$F_p^e$	$F_p^e$	$F_e^e P_e^f$
A'	3	2	2	2 or 1	2 2
A''	3	1	2	0 or 1	2 2

a = assumed  $C_s$  molecular symmetry

b = faces perpendicular to infrared beam

c = C site symmetry,  $C_{2v}^2$  space group symmetry

d =  $C_s$  site symmetry,  $C_{2v}^2$  space group symmetry

e  $F_p(e)$  = predicted (experimental) number of factor group components

f  $P_e$  = experimental number of unique band polarizations

Table 3. Fundamental Vibrational Modes<sup>a</sup> of Crystalline Acetic Acid -d<sub>0</sub>

Assignment	Molecular Symmetry Species	Reported Frequency <sup>15</sup>	This Work <sup>b</sup>		
			Polarizer Out	$\alpha$	$\alpha + 90$
$\nu_{OH}$	A'	2875	2910	2910	2910
$\nu'_S CH_3$	A'				
$\nu_S CH_3$	A'				
$\nu_{C=O}$	A'	1648	1653.2	1652.5	1652.9
$\delta'_S CH_3$	A'	1448-39			
$\delta_S CH_3$	A'	1356	1347.0	1348.0	1354.0
$\delta_{OH}$	A'	1418	1415.6	1402.4	1417.9
$\nu_{C-O}$	A'	1248	1270.8	1268.3	1272.8
$\rho_S CH_3$	A'	1022	1017.6	1018.3	1016.7
$\nu_{C-C}$	A'	908	911.4	908.9	911.6
$\delta_{COO}$	A'	635	629.6	627.9	631.0
$\delta_{CCO}$	A'	450	452.3	452.6	451.4
<hr style="border-top: 1px dashed black;"/>					
$\nu_a CH_3$	A''				
$\delta_a CH_3$	A''	1448-39			
$\rho_a CH_3$	A''	1049	1044.2	1043.3	1044.0
$\gamma_{OH}$	A''	923	~908	908.9	897.1
$\gamma_{CCO}$	A''	592		588.6	593.6

a = all frequencies in  $cm^{-1}$

b = 193°K

Table 4. Fundamental Vibrational Modes<sup>a</sup> of Crystalline Acetic Acid -d<sub>1</sub>

Assignment	Molecular Symmetry Species	Reported Frequency <sup>15</sup>	This Work <sup>b</sup>		
			Polarizer Out	$\alpha$	$\alpha + 90$
$\nu_s'CH_3$	A'	3040			
$\nu_aCH_3$	A''	3000			
$\nu_sCH_3$	A'	2950	2927		
$\nu OD$	A'	2194	2202.7	2204.2	2200.5
$\nu C=O$	A'	1644,1629		1644.4	1644.3
$\delta_sCH_3$	A'	1395,1385		1373.8	1394.7
$\nu C-O$	A'	1322	1318.2	1316.8	1318.9
$\delta OD$	A'	1972	1067.8	1067.9	1066.4
$\rho_aCH_3$	A''	1046	1044.7	1043.5	1044.8
$\rho_sCH_3$	A'	1010	1007.0	1007.1	1006.3
$\nu C-C$	A'	857		854.6	855.1
$\gamma OD$	A''	678	671.6	671.8	672.1
$\delta COO$	A'	611,606	606.2	604.2	607.8
$\gamma CCO$	A''	580		581.7	582.4
$\delta CCO$	A'	446		446.6	445.6

a = all frequencies in  $cm^{-1}$ 

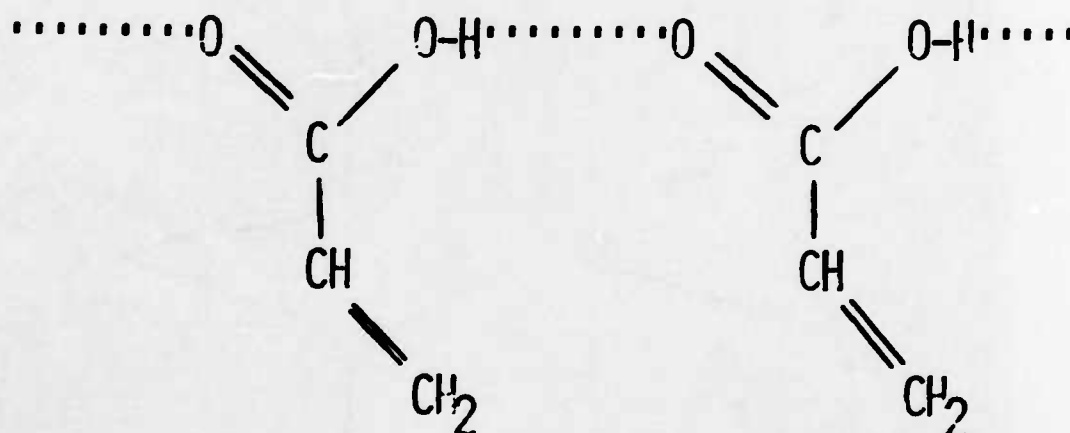
b = 147°K

Table 5. Fundamental Vibrational Modes<sup>a</sup> of Crystalline Acetic Acid-d<sub>4</sub>

Assignment	Molecular Symmetry Species	Reported Frequency <sup>15</sup>	This Work <sup>b</sup>	
			$\alpha$	$\alpha + 90$
$\nu_{OD}$	A'	2187	~2195	~2190
$\nu_{C=O}$	A'	1640	~1641	~1641
$\nu_{C-O}$	A'	1340		
$\delta_{OD}$	A'	1100	1095.5	1101.1
$\delta_s CD_3$	A'	1045	1043.4	1042.9
$\delta'_s CD_3$	A'	1035		
$\rho_s CD_3$	A'	841	838.7	839.6
$\nu_{C-C}$	A'	808	807.8	809.4
$\delta_{COO}$	A'	591	591.0	592.5
$\delta_{CCO}$	A'	399	399.6	399.4
<hr style="border-top: 1px dashed black;"/>				
$a_{CD}$	A''	1035		
$\rho_a CD_3$	A''	924	924.4	926.0
$\gamma_{OD}$	A''	672	669.6	669.7
$\gamma_{CCO}$	A''	505		

a = all frequencies in cm<sup>-1</sup>

b = 95°K



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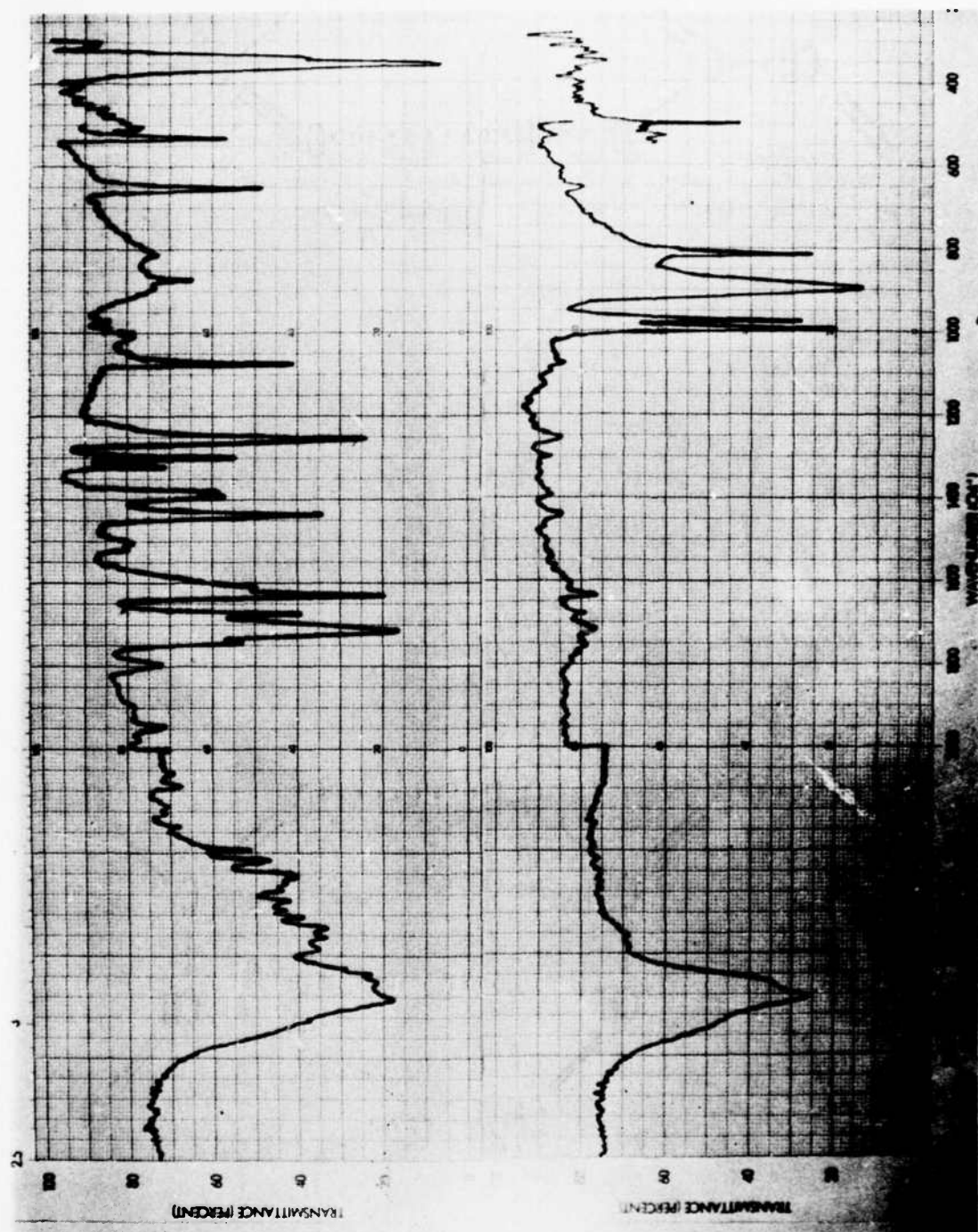


Figure 2. Polarized Mid-Infrared Spectra of Acrylic Acid. The two spectra differ by rotation of the polarizer by  $90^\circ$ . The break in the spectra at about  $500\text{ cm}^{-1}$  indicates a longer pathlength below this value.

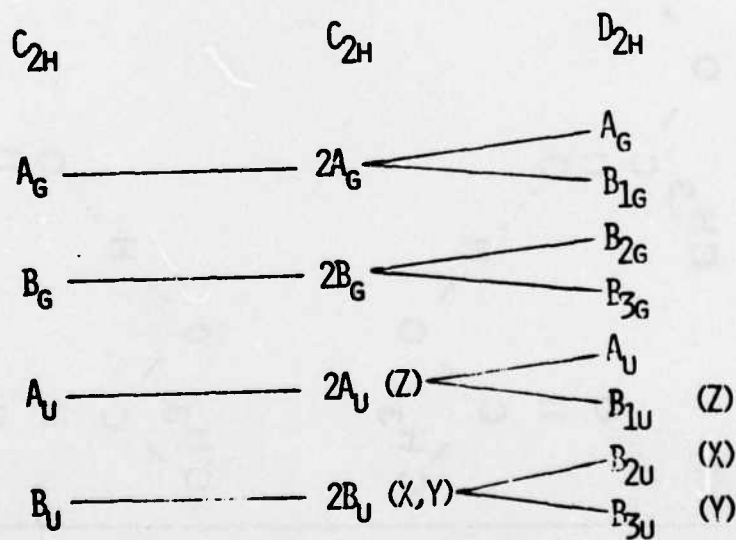
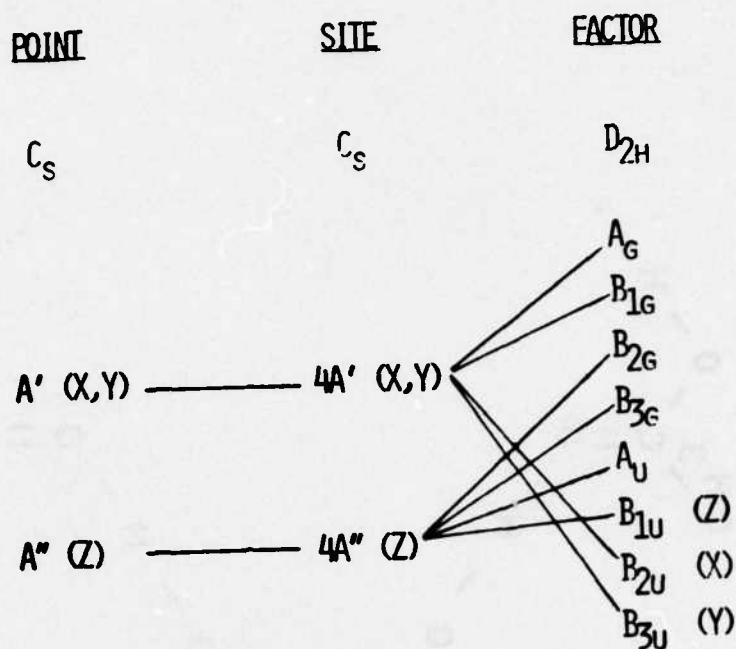


Figure 3. Correlation Diagrams for Acrylic Acid. The upper diagram represents the correlation in terms of monomer units and the lower represents the correlation in terms of dimer units.



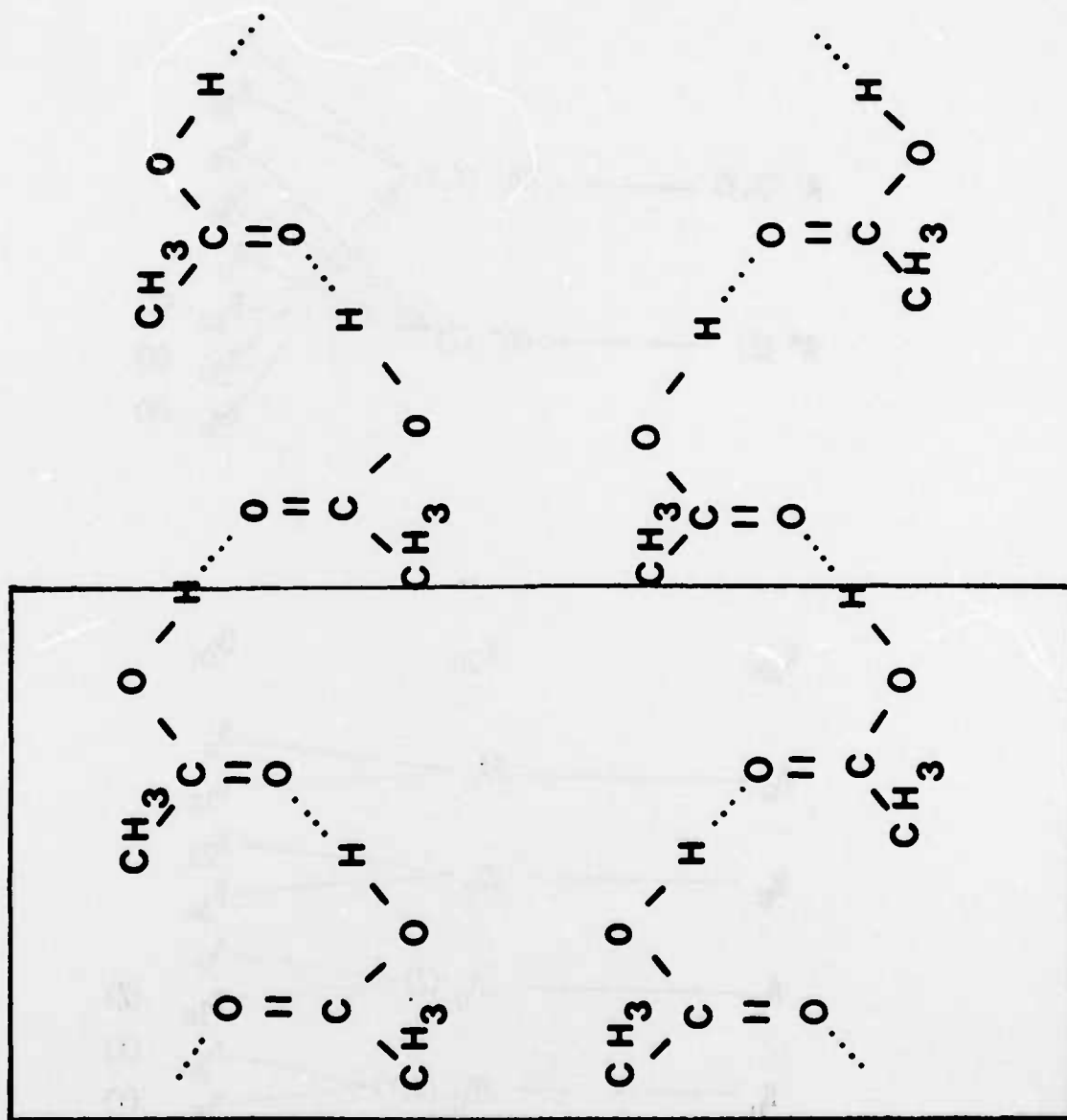


Figure 4. Projection of the unit cell of acetic acid on the *ab* plane. The polymer chains are spiral in nature.

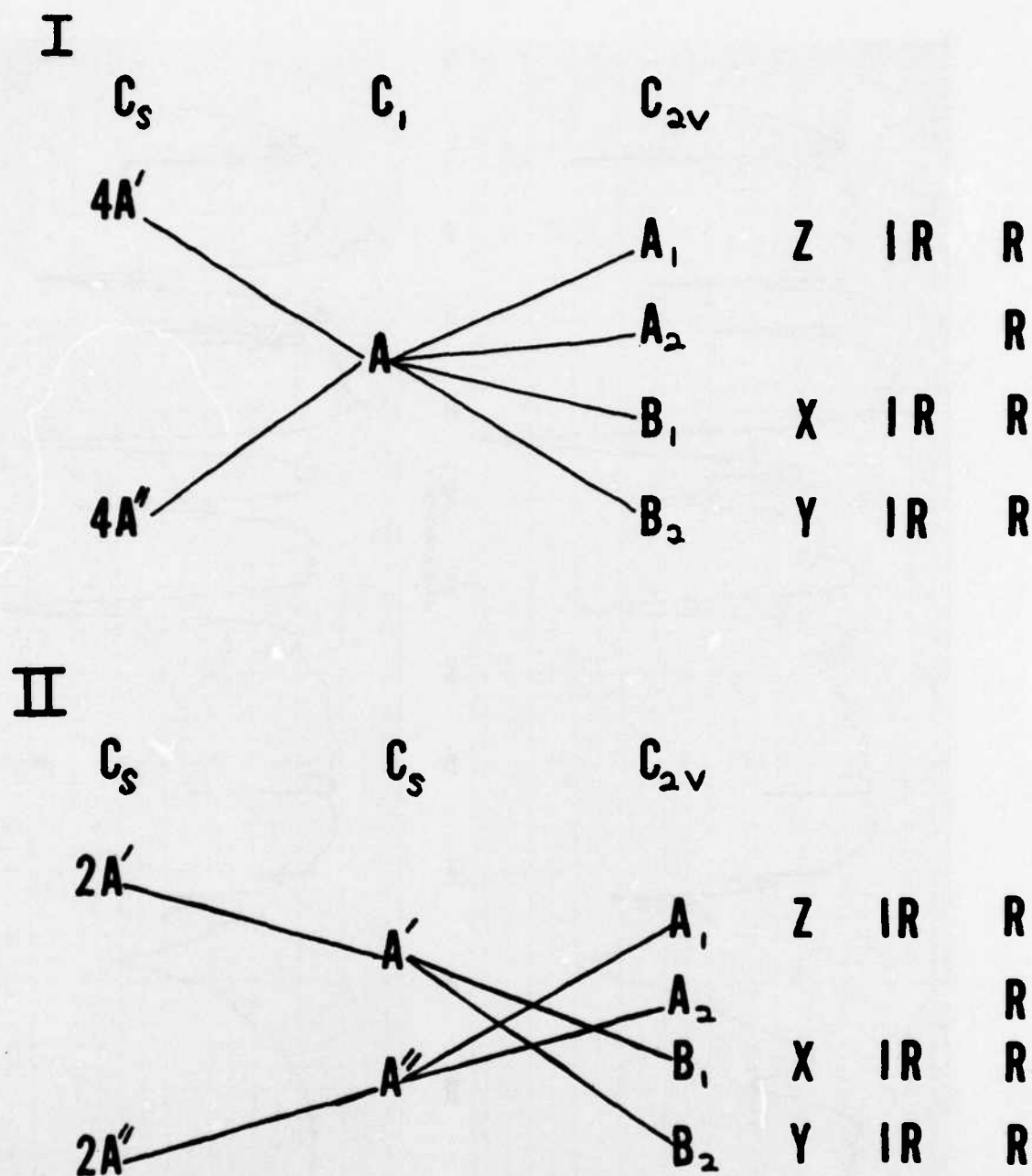


Figure 5. I. Correlation diagram for the four molecule Bravais cell of crystalline acetic acid.  
 II. Correlation diagram for two molecule chain unit cell of crystalline acetic acid.

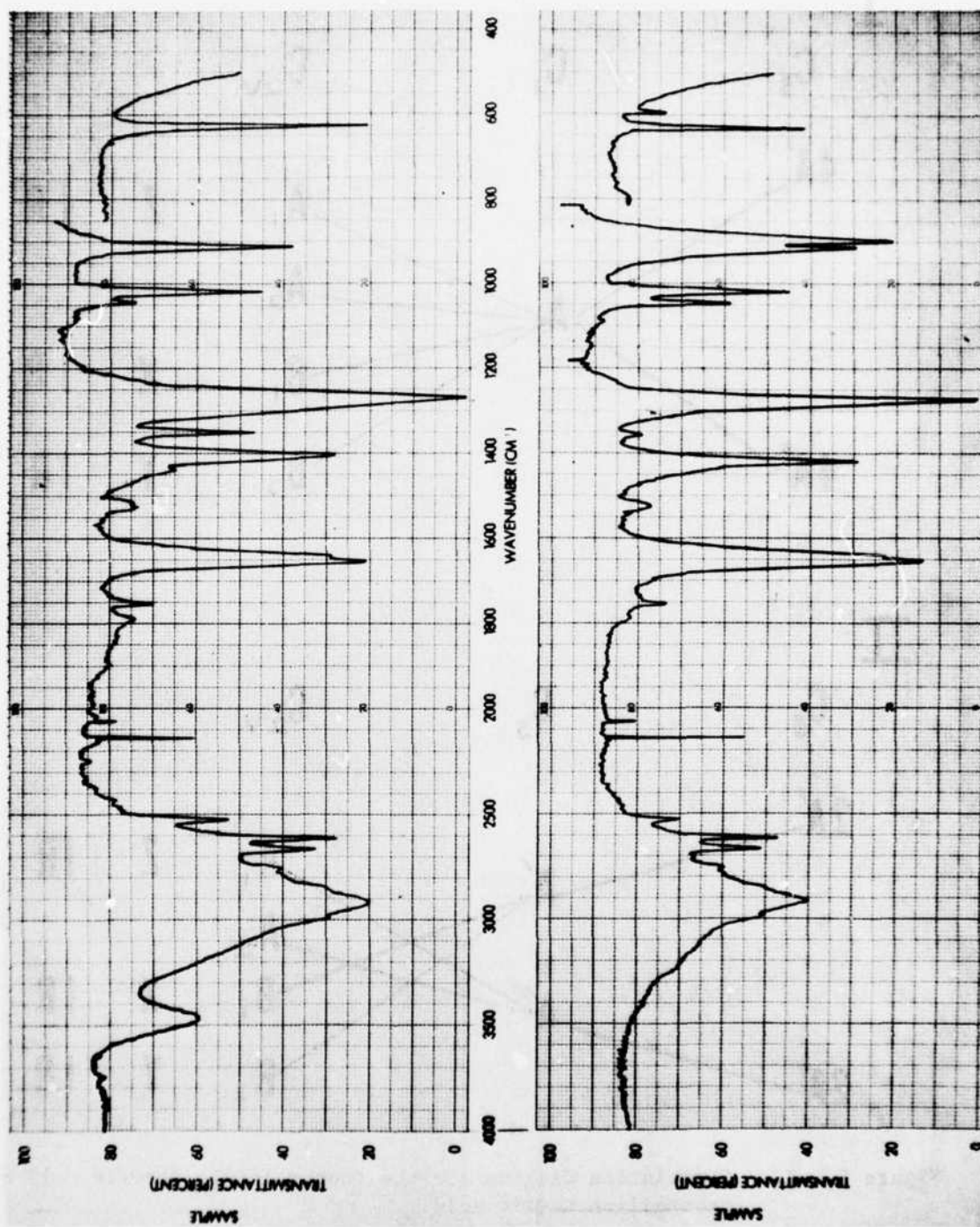


Figure 6. Polarized infrared spectrum of crystalline acetic acid-d<sub>4</sub> at 190°K. The two traces differ by a 90° rotation of the polarizer.

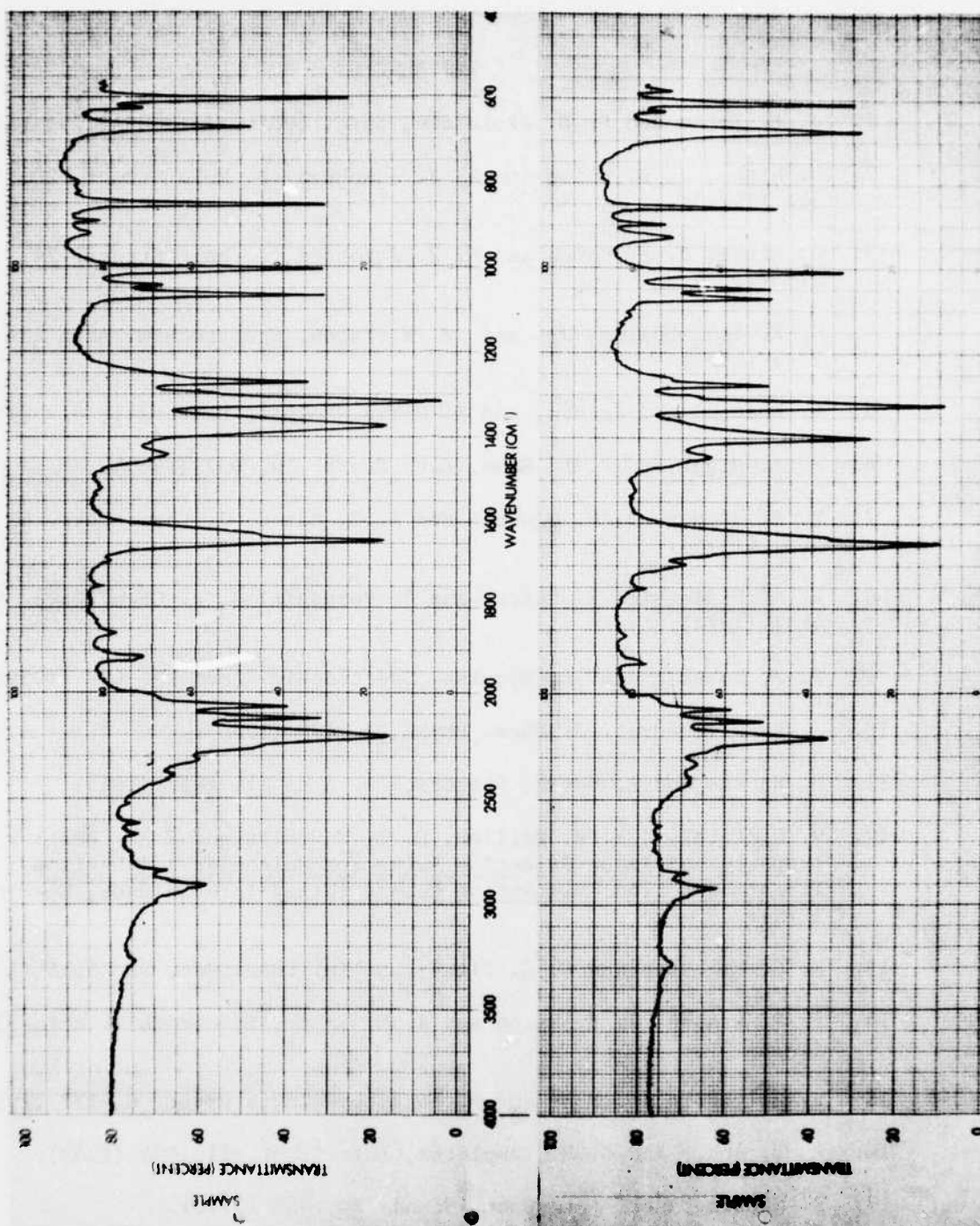


Figure 7. Polarized infrared spectrum of crystalline acetic acid-d<sub>1</sub> at 147°K. The two traces differ by a 90° rotation of the polarizer.

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